



Erosion of the molecular network in the amorphous layers of polyethylene upon high-strain deformation



Zbigniew Bartczak^{a,*}, Magdalena Grala^a, Emmanuel Richaud^b, Krystyna Gadzinowska^a

^a Centre of Molecular Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

^b Arts et Metiers ParisTech, Laboratoire de Procédés et Ingénierie en Mécanique et Matériaux (PIMM), CNRS, UMR 8006, 151 Boulevard de l'Hopital, 75013 Paris, France

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ABSTRACT

Samples of linear polyethylene, neat and crosslinked by irradiation with electron beam, were subjected to heavy plastic deformation by plane-strain compression up to the true strain exceeding 2 (deformation ratio $\lambda > 8$) at room temperature. Structural studies of deformed samples and investigation of long-term strain recovery demonstrated that the deformation of the neat, non-crosslinked HDPE is completely reversible above the melting point of the crystalline phase, provided that the applied true strain does not exceed $e = 1.0$ ($\lambda = 2.7$). At higher applied strains, $e > 1$, an irreversible deformation component emerged gradually, and at $e = 2.1$ ($\lambda = 8.2$), the permanent, truly irreversible, residual strain was approx. $e_{res} = 0.36$ ($\lambda = 1.4$). In contrast, samples of crosslinked HDPE above T_m exhibited complete reversibility of deformation, irrespectively of an applied strain, and $e_{res} \approx 0$. The source of permanent irreversible strain component in neat HDPE is a deformation-induced partial destruction of the molecular network of entangled chains within amorphous interlamellar layers. The principal mechanism found was chain disentanglement, which was supplemented by a very limited chain scission. In the case of crosslinked materials, the dense and relatively homogeneous molecular network appeared robust enough to avoid any damage. Consequently, the strain appeared here fully reversible upon melting of crystalline phase.

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1. Introduction

Semicrystalline polymers can deform to very high strains. Their deformation is a complex and multi-level process due to complicated hierarchical structure. A variety of mechanisms operate at different levels of the structure and the process of deformation is strongly dependent on the underlying microstructure of the material. Any macroscopically homogenous deformation is accommodated by cooperative action of these mechanisms in the heterogeneous multi-level structure.

The microstructure of semicrystalline polymer is commonly described by a two-phase model consisting of randomly oriented crystalline lamellae stacks intercalated with amorphous layers. At this level, the basic micromechanisms of deformation of crystals and amorphous phase are considered. It has been well established that the principal mechanisms involved in the plastic deformation of polymer crystals are crystallographic in nature, primarily

crystallographic slip that appears active at all strain levels [1,2]. For the amorphous phase, it was found that the shear of amorphous interlamellar layers was the principal deformation mechanism. It plays a very important role in the deformation sequence, not only allowing for a high orientation of amorphous component, but also influencing deeply the deformation of crystalline phase, since both phases are intimately connected through many chains crossing the crystalline/amorphous interface, therefore both components can deform only simultaneously and consistently [2]. This implies that amorphous phase, in spite of compliance much higher than crystals (at $T > T_g$), can deform independently only in a very limited extent. Consequently, at the initial and moderate stages, deformation of amorphous layers merely follows deformation of adjacent crystalline lamellae [3–6]. Situation changes at high strains, when increasing rubber-elastic stresses generated upon advanced shear deformation of amorphous layers become higher than stresses accompanying deformation of crystalline phase, much less dependent on strain [7]. From this point on, the interlamellar shear of amorphous component takes control over the process of further deformation, and deformation of crystals now only accommodates to strain increment of the amorphous phase. During the early and

* Corresponding author.

E-mail address: bartczak@cbmm.lodz.pl (Z. Bartczak).

moderate stages of deformation, crystals become distorted but the crystalline lamellae remain undestroyed, whereas at larger strains, the original crystalline microstructure frequently breaks down due to advanced slip and a high stress generated in adjacent amorphous layers and transmitted to crystals. Consequently, a new fibrillar structure is formed [8,9].

The mechanical response of an amorphous phase is determined by its topological structure, including chains crossing interfaces with neighboring lamellae (as e.g. tie-molecules, loose loops or cilia) and a molecular network of entangled chains [10]. In this molecular network, chain segments immobilized at interfaces constitute *quasi*-solid crosslinks, while entanglements represent crosslinks of a certain mobility, which ultimately, at some conditions, can be even resolved (chains disentangled). It is already well understood that strain hardening in amorphous polymers originates from the network structure [11–13]. The same is actually true for semicrystalline polymers, since their deformation can be considered as a simultaneous deformation of two co-continuous interlaced network-like structures: a skeleton made up of crystallites interconnected with the interlamellar layers of entangled amorphous phase [4], deformation of which is supposed to proceed in a similar fashion as deformation of an amorphous polymer, including the rubber-like behavior above the glass transition temperature. Deformation of molecular network within amorphous layers is finite, limited by the length of segments between crosslinks, primarily entanglements. Deformation of amorphous layers should manifest then in a very high stress response to large strain [7], especially when approaching the network extensibility limit, and high reversibility of deformation, which in fact is frequently observed experimentally [10,14,15].

Strobl et al. [4–6,16,17] demonstrated that the properties of the molecular network influence deeply the deformation behavior of semicrystalline polymers. They proposed a strain-controlled deformation scheme of semicrystalline polymers, in which two of the critical strains, controlling the deformation sequence (points C and D at the true strain around $e = 0.6$ and $e = 1$, respectively [4]), are related to the response of the molecular network. According to this scheme, stretching of the sample leads to a gradual orientation of the amorphous chains along the drawing direction that obviously decreases the entropy of the amorphous phase. A retracting force is generated since the system tends to recover an isotropic state of optimized entropy [18]. This force generated in the deformed network of entangled chains within interlamellar layers is transferred to neighboring crystallites by macromolecular chains linking both phases. At the point C, at true strain of approx. 0.6, the stress acting on crystalline lamellae reaches a critical value above which they are no longer stable and undergo fragmentation, which eventually leads to partial destruction of the initial morphology and replacing it by the fibrillar structure. Finally, with a further progress of deformation, the entangled network of amorphous phase approaches its extensibility limit, which results in a strong rise of the stress. That leads to another transition, manifesting in a decreasing amount of strain recovered upon sample unloading, found above the true strain of 1–1.2 ($\lambda \sim 3$; point D of the Strobl's scheme). This transition was postulated to be a result of intensified crystal fragmentation and presumably chain disentanglement beginning in amorphous phase that should lead to a partial disintegration of the molecular network [4]. Our previous studies supported the Strobl's view on the deformation sequence and confirmed a direct correlation between concentration of entanglements and the deformation behavior, especially at high strains, in the strain hardening range, [3,10,15,19,20]. Model calculations [7] as well as experimental studies of the post-deformation relaxation behavior of compressed polyethylene [10] indicated that the rubber-like network stress, a sub-component of the observed elastic part of

the stress, increases substantially at high strains, above the true strain of $e = 1.0$, and is evidently the main source of the strong strain hardening of the sample. Moreover, the contributions of rubber-like recoverable deformation and permanent plastic flow depend directly on the actual network density, which is possibly reduced at high strain due to resolving of entanglements [19]. Investigation of a broad range of samples of polyethylene homo- and copolymers [10,15] demonstrated that the response of the molecular network of entangled chains in amorphous layers change significantly above of $e = 1$ for all materials studied. In samples deformed below this strain, a significant part of the applied strain appeared recoverable, especially upon heating close to the melting point (even a nearly complete recovery was observed in an ethylene copolymer of very low crystallinity). Above $e = 1$, the contribution of the permanent (unrecoverable) strain component was observed to increase gradually with an advance of applied strain. Such behavior could suggest a strain-induced progressive destruction (erosion) of the molecular network, beginning at $e = 1$. The postulated mechanism of network erosion was either (i) disentanglement or (ii) scission of highly stretched chains, both leading to some reduction of the network density and hence a partial relaxation of the network. That relaxation allows further deformation of the amorphous phase, already deformed nearly to its extensibility limit. Even if the mechanism (i) involving disentanglement sounds attractive, it may not be a principal mechanism because large translations of chains is required to resolve completely an entanglement knot, especially when located in the mid-length of the chain and the molecular weight is high. The flow produced by interlamellar shear can appear then sufficient only for resolving entanglements of relatively short chains or those entanglements that are located close to the chain ends in long chains. On the other hand, it seems that the complete resolution of numerous entanglements is not required to change the network properties, and much more probable translations of mobile entanglements along the chain can be sufficient to increase distances between crosslinks and modify response of the network. The second postulated mechanism – the scission of primary bonds in the main chain needs a high local stress along the chain in order to break the very strong C–C bonds in the chain backbone. This implies a very high stress in the sample, which is possible only in the final deformation stages of the most intense strain hardening and fracture. Chain scission was detected experimentally in several semicrystalline polymers to occur mainly on fracture. Both direct (ESR detecting directly the free radicals, see e.g. Refs. [21,22]) and indirect methods (as reduction in average molar mass [23–25] or increase of concentration of end-groups determined with IR spectroscopy [23,26–28]) were used. For plastic deformation prior to fracturing, the chain scission mechanism was excluded as a major contributor to the plastic deformation [29–31], although some reports indicated its occurrence upon a very heavy deformation [32].

A large number of material models were developed to predict the mechanical response of amorphous polymers (see e.g. Ref. [33] for the review). More recently, the mechanical behavior of semicrystalline polymers has been also extensively modeled (see e.g. Ref. [34] for references). Many efforts have been carried out to describe their complex mechanical behavior at large strains, considering also a possible contribution of chain disentanglements. For example, the model developed recently by Billon predicts that entanglements initially are not mechanically active and act as crosslinks at low stress/strain, then with increasing strain energy they gain a certain level of mobility that induces visco-elasticity and from a certain limit of energy they gain in mobility, which corresponds to disentanglement and visco-plasticity at high strain [34,35].

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